

# The Effect of Polymer Surface Modification Via Interfacial Polymerization on Polymer–Protein Interaction

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Received 21 February 2008; accepted 2 November 2008

DOI 10.1002/app.29606

Published online 9 February 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Membrane separation is an important processing technology used for separating food ingredients and fractionating value-added components from food processing byproducts. Long-term performance of polymeric membranes in food protein processing is impeded by the formation of fouled layers on the membrane surface as a result of protein adsorption onto the membrane surface. Surface modification of synthetic membranes, i.e., changing surface characteristics to reduce protein adsorption permanently, is one of the innovative ways of reducing the fouling of membrane surfaces. In this study, surface modification of flat-sheet ultrafiltration membrane, polyethersulfone (PES), was investigated in improving the hydrophilicity of PES surfaces, thereby reducing adsorption of the protein caused by hydrophobic–hydrophobic interaction between the protein and the membrane. Hydrophilic polymer grafting through thin-film composite using interfacial polymerization was employed to improve the hydrophilicity of the commercial PES membranes. Poly(vinyl alcohol), poly(ethylene glycol), and chitosan were chosen as hydrophilic poly-

mers to graft on PES membrane because of their excellent hydrophilic property. Modified PES membranes were characterized by contact angle, FTIR, XPS, and AFM. Contact angles of modified PES membranes were reduced by 25 to 40% of that of the virgin PES membrane. XPS spectrum supported that the PES membranes were successfully modified by interfacial polymerization. Tapping-mode AFM was used to examine the changes in surface topography of modified PES membranes. The PES membranes modified by interfacial polymerization showed lower roughness (from 1.2 to 2.0 nm) than that of virgin PES membrane (2.1 nm). The results of these instrumental analyses indicated that the PES membranes were successfully enhanced hydrophilically through interfacial polymerization. The protein adsorption on the modified membranes was reduced by 30 to 35% as a result of surface modification of the PES membranes using interfacial polymerization technique. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1704–1715, 2009

**Key words:** composites; FTIR; AFM; XPS; membranes

## INTRODUCTION

Many past researches have revealed that the increase in hydrophilicity of membranes significantly reduce the membrane fouling because of the decrease in the hydrophobic interaction between protein and membrane surface.<sup>1,2</sup> Hydrophilic membranes are often preferred membranes for processing aqueous protein solutions, as fouling is generally less severe than hydrophobic membranes. Unfortunately, most commercial membranes are relatively hydrophobic because hydrophilic membranes have drawbacks in their mechanical, thermal, and chemical stability.

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*Journal of Applied Polymer Science*, Vol. 112, 1704–1715 (2009)  
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Hydrophobic polymeric membranes have been commonly used in ultrafiltration systems to concentrate and fractionate proteins.

Surface modification of polymeric membrane can enhance membrane performance such as permeation flux, efficiency, and selectivity through improving properties of membrane surface. For example, surface modification of hydrophobic membranes to hydrophilic ones result in the reduction of the hydrophobic interactions between proteins and membrane surfaces, thus reducing protein adsorption and membrane fouling. The most effective way of improving hydrophilicity of virgin hydrophobic membranes is to incorporate hydrophilic polymers or functional groups on the virgin membrane surfaces. The incorporation of hydrophilic polymer through blending,<sup>3,4</sup> coating,<sup>5</sup> and surface grafting<sup>6–8</sup> has been developed to improve the protein adsorption resistance and permeation property of polymeric membranes.

It is recognized that the extent of protein adsorption depends on the various types of interactions

between protein molecules and membrane surface, such as van der Waals interaction, electrostatic interactions, hydrophobic interaction, dipole–dipole interaction, and hydrogen bonding.<sup>9</sup> Protein adsorption on the polymeric membrane due to the hydrophobic interaction between the membrane surface and protein molecules is one of the most significant factors in causing protein-adsorption-induced membrane fouling. Therefore, reduction in hydrophobicity on the membrane surface through the incorporation of hydrophilic polymers or functional groups can result in substantial fouling reduction.<sup>1</sup> With surface modification, two distinct layers were made of two different polymeric materials. The thin surface layer governs the selectivity, flux, and adsorption of solute, whereas the thicker substrate layer provides mechanical strength and chemical stability. The more hydrophilic membrane surface not only reduces fouling but also makes cleaning of the hydrophilized membrane easier because the adsorbed protein molecules can be easily removed from the hydrophilic surface because of the weaker attachments.<sup>8</sup>

The hydrophilic polymer grafting using UV/ozone and the thin-film composite (TFC) by interfacial polymerization had been studied to improve the hydrophilicity of the polyethersulfone (PES) membrane surface.<sup>10–12</sup> These polymer grafting methods have been shown to be successful in increasing the surface hydrophilicity and the permeability and decreasing the membrane fouling during the protein filtration. In this study, interfacial polymerization technique was employed to generate hydrophilicity on the commercial PES membranes. Interfacial polymerization is a powerful technique for fabrication of composite membranes with a very thin active layer. Although it had been used for the membranes of reverse osmosis, interfacial polymerization technique can also be useful for nanofiltration and ultrafiltration.<sup>13,14</sup> Interfacial polymerization technique is based on a polycondensation reaction that takes place at the interface between two immiscible phases, one is organic solvent and the other is water phase. A fast polymerization reaction often occurs between two reactive monomers at the interface of two immiscible solvents each containing one of the monomers (for example, polyamine in water phase and polyacyl chloride in organic solvent), and the polymer precipitates quickly, forming a thin dense polyamide film.<sup>15–17</sup> Because the thin active layers formed by interfacial polymerization contain hydrophilic polymers, it would reduce the protein adsorption and membrane fouling.

In this study, poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG), and chitosan were used as hydrophilic polymers for grafting because of their excellent hydrophilicity. PVA has been well known for its excellent film-forming property, emulsifying

property, and minimal cell and protein adhesion property.<sup>18,19</sup> PVA is also resistant to oil and solvent. PEG showed extraordinary antifouling property to protein adsorption because of its hydrophilicity, flexible long chains, large exclusion volume, and unique coordination with surrounding water molecules in an aqueous solution.<sup>20</sup> Chitosan is a linear polyelectrolyte carrying positive charges and has been identified as a nontoxic, biodegradable, biocompatible, and hydrophilic polysaccharide. Chitosan-based membranes have been used for protein separations.<sup>21</sup>

## EXPERIMENTAL

### Materials

The flat sheet ultrafiltration membrane, PES (YMPWSP3001), was purchased from Sterlitech Corporation (Kent, WA). Molecular weight cutoff (MWCO) of flat sheet PES membrane was 20,000. Terephthaloyl chloride (TC), *m*-phenylenediamine, PEG 2000, and PVA were purchased from Sigma-Aldrich (St. Louis, MO). Chitosan (MW 300,000, degree of deacetylation 90%) was purchased from Kunpoong Bio (Jeju, South Korea).

### Thin-film composite by interfacial polymerization

The polymeric membranes were immersed in 1% (w/v) TC in benzene for 20 min. After 20 min, the membranes were exposed in an aerator for 1 min to remove excess TC solution from the membrane surface. Membranes were then immersed into the aqueous solution containing 1% *m*-phenylenediamine and 1% hydrophilic polymers such as PVA, PEG 2000, and chitosan to form a composite membrane surface layer by interfacial polymerization (Table I). The fabricated PES membranes were rinsed with deionized water and then dried at room temperature for 24 h.

### Contact angle measurement

The contact angles of the unmodified and modified PES membranes were measured by sessile drop method on a VCA Optima surface analysis system (Advanced Surface Technology, Billerica, MA). A 28-gauge blunt-tip needle was used for dispensing a 2  $\mu$ L deionized water droplet onto the surface of membrane samples. Five measurements were made for each sample to determine the average and standard deviation.

### ATR-FTIR spectra

ATR-FTIR spectra of unmodified and modified PES membranes were measured with a Thermal Nicolet Nexus 670 FTIR system with an ATR accessory. The ATR accessory contained a ZnSe crystal (25 mm  $\times$

5 mm × 2 mm) at a nominal incident angle of 45°, yielding about 12 internal reflections at the sample surface. All spectra were recorded with 256 scans at 4.0 cm<sup>-1</sup> resolution at room temperature.

### X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) spectra of virgin and modified PES membranes were recorded with a Kratos XSAM 800 XPS using a monochromatic Al K $\alpha$  X-ray source (1486.6 eV photons) at 350 W and 15 kV. The take-off angle was 90°. Analysis of the high-resolution XPS spectra for unmodified and modified PES membranes was based on the Ref.<sup>22</sup> In all cases, a Gaussian peak shape was used, and the analyses were performed with the binding energies and full-width-at-half-maxima of the peaks kept constant at the literature values but with the intensities varied.

### Atomic force microscopy

The surface topography and phase image of modified PES membrane were measured by tapping mode atomic force microscope (AFM; Multimode SPM, Nanoscope IIIa; Digital Instruments, Woodbury, NY) with a silicon probe with a spring constant of 40 N/m and a resonance frequency of ~300 kHz. The scan rate was in the range 0.5–1.2 Hz. Several specimens were scanned to obtain their morphologies. The root mean square roughness was also characterized to gain an understanding of membrane surface characteristics.

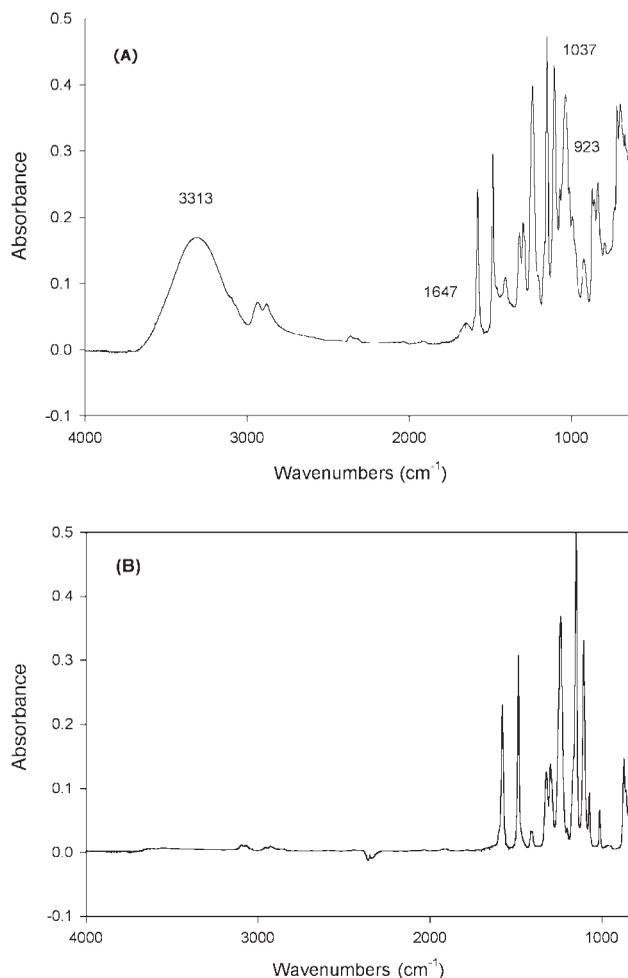
### Protein adsorption on modified PES membranes

Static adsorption of  $\beta$ -lactoglobulin on the modified PES membrane surface was studied by using UV-vis spectrophotometer via the absorbance at 280 nm to show the decreased protein adsorption by surface modification. For this study, the concentration of  $\beta$ -lactoglobulin of 2.5 mg/mL and a solution of pH 3.0 were chosen because the maximum adsorption was observed under this condition; the detailed procedure for the protein adsorption experiments including materials and methods is documented in the previous report.<sup>23</sup>

## RESULTS AND DISCUSSION

### Characterization of virgin PES membrane using ATR-FTIR

In the commercial manufacture processing of polymeric membranes, preservatives have been commonly used to stabilize membranes to prevent the membranes from microbial attack and to extend their shelf life. As shown in Figure 1(A), preservatives present a very strong band at 3313 cm<sup>-1</sup> and three bands at 1647, 1037, and 923 cm<sup>-1</sup>, which are

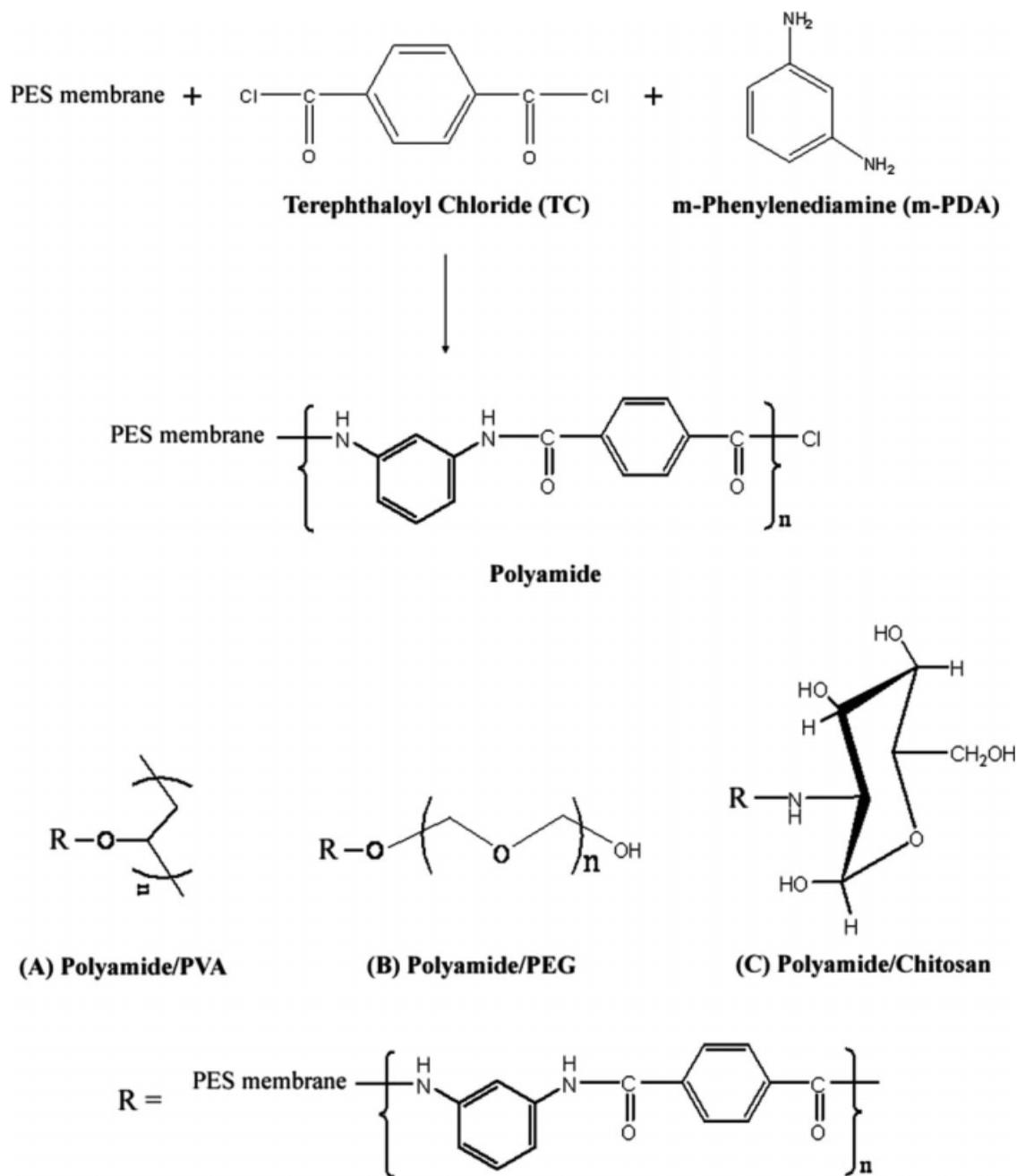


**Figure 1** ATR-FTIR spectra of the PES membrane (A) before washing and (B) after washing with DI water.

the same spectra of the preservatives in the previous research.<sup>24</sup> Preservatives were washed out with DI water and dried at room temperature for several days for the characterization of native PES membranes. All PES membranes used for surface modification were washed with DI water for 24 h to remove the preservatives and dried at room temperature. The spectra of the washed PES membrane have no strong band at 3400 cm<sup>-1</sup>, which indicates the aliphatic C–H stretching, but two small bands associated with aromatic C–H vibration are present at 3095 and 3069 cm<sup>-1</sup> as shown in Figure 1(B). There is no band around 3500 to 3600 cm<sup>-1</sup>, which is associated with the O–H stretching vibration of water molecules. Therefore, this IR spectrum supports that PES membrane was dried completely after washing out the preservatives.

### Interfacial polymerization

Surface modification of PES membrane was carried out by fabricating hydrophilic polymers/polyamide

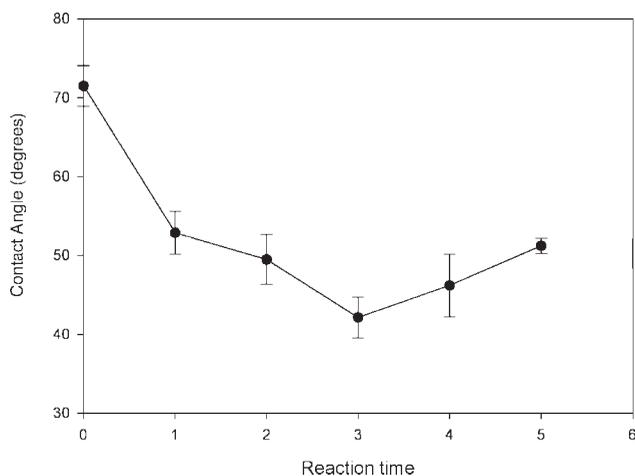


**Figure 2** Reaction scheme for the preparation of the composite membranes with hydrophilic polymers by interfacial polymerization: (A) PVA/polyamide, (B) PEG/polyamide, and (C) chitosan/polyamide.

thin layer on the PES membrane surface by interfacial polymerization. Interfacial polymerization is an effective method for the fabrication of composite membranes with very thin active layer (usually 10 to 20 nm). The schematic of the interfacial polymerization is shown in Figure 2. To optimize the reaction time in the interfacial polymerization processing, contact angle changes were measured by varying reaction times between organic solvent (terephthaloyl chloride in benzene) and water phase (*m*-phenylenediamine). As shown in Figure 3, contact angle was decreased with the reaction time, and minimum

contact angle was observed at 3 min. After 3 min, however, the contact angle was increased again over reaction time. Therefore, all the interfacial polymerizations were reacted for 3 min.

After the interfacial polymerization reactions, contact angles of the modified PES membranes were measured and compared with that of virgin PES membrane. As shown in Figure 4, contact angles of PES membranes were reduced from 25 to 40% by surface modification. This observation confirms that the PES membranes were modified by the formation of polyamide layers on the membrane surfaces.



**Figure 3** Contact angle changes by reaction time in interfacial polymerization.

Lower contact angles indicate that the modified membranes were changed to more hydrophilic surface, and lower protein adsorption is expected because of the reduced hydrophobic interaction.

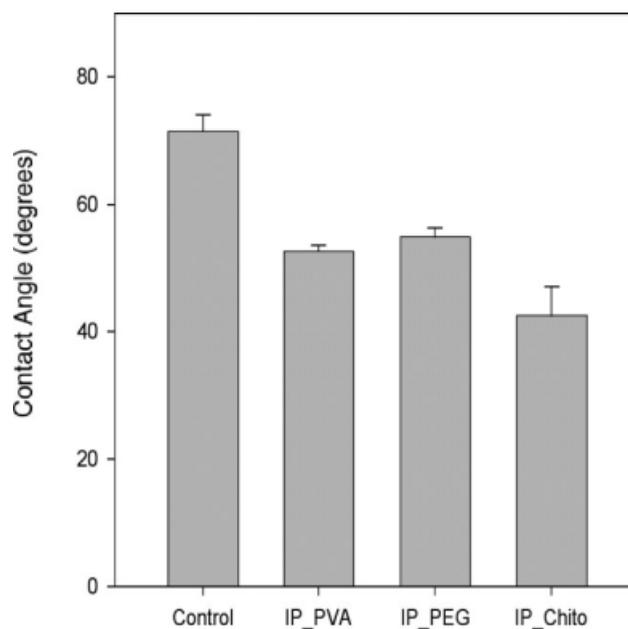
### Characterization of modified PES membranes

To understand the interactions between the modified membrane surface and protein molecules, it is important to have good knowledge of the various surface properties of the modified PES membranes. The surface topography, roughness, wettability, and chemical composition of modified PES membranes were characterized by AFM, contact angle, and XPS. ATR-FTIR was used to characterize the modified functional groups on the PES membrane surface.

Electron spectroscopy for chemical analysis (ESCA), also known as XPS, is a powerful technique for characterizing the chemical composition of the top few atomic layers at the surface of a solid. A beam of X-rays impinging on a surface causes the ejection of electrons from core levels in the atoms because of the photoelectric effect as shown in Figure 5. When a monochromatic source of X-rays of known energy ( $1253.6 \text{ eV}$  for  $\text{Mg K}\alpha$  and  $1486.6 \text{ eV}$  for  $\text{Al K}\alpha$ ) is used, the binding energy can be determined if the kinetic energy of the electrons is measured. The kinetic energy of the ejected electrons is equal to the difference between the energy of the X-rays and the binding energy,  $E_b$ :

$$E_k = h\nu - E_b$$

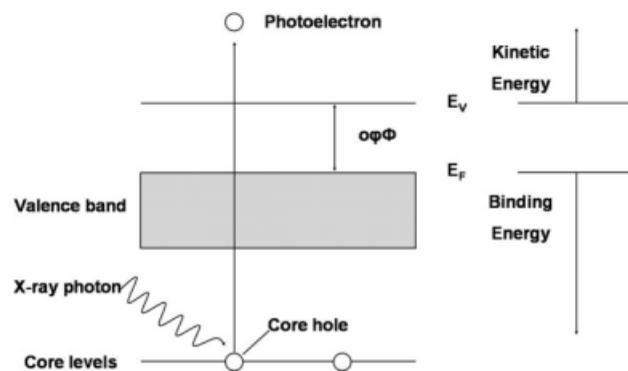
where  $h$  is the Planck constant,  $\nu$  is the wavelength of the incident photons,  $E_b$  is the energy of the core level from which the electron is ejected. ESCA can not only give the elemental composition of a surface (C, O, N, S, etc.) but also provide insights into the



**Figure 4** Contact angle of modified PES membranes.

chemical bonding at the surface. XPS is a highly surface-specific analytical technique used to obtain the chemical structure and atomic composition of a material.

To obtain further information about the composition change of the modified PES membrane surface, unmodified and modified PES membranes were subjected to XPS. First of all, the surface compositions and the atomic percentages of virgin PES membrane are shown in Table II and shown in Figure 6. As shown in Table III, the atomic percentages of unmodified PES membrane were 71.75% for carbon, 21.99% for oxygen, and 5.32% for sulfur, respectively. The ratio of oxygen to carbon is 0.306, and the ratio of sulfur to carbon is 0.074. Figure 6 shows the high-resolution  $\text{C}_{1s}$ ,  $\text{O}_{1s}$ ,  $\text{N}_{1s}$ , and  $\text{S}_{2p}$  XPS spectra of virgin PES membrane surface layer. In case of the virgin PES membrane surface layer, the  $\text{C}_{1s}$  core-level spectrum can be deconvoluted into three peak components. Carbon atoms at the PES surface



**Figure 5** Photoelectric effect of XPS.

**TABLE I**  
Experimental Design for Surface Modification of PES Membrane

Sample no.	Description of modification
No. 1	Virgin PES membrane
No. 2	Modified with 1% PVA
No. 3	Modified with 1% PEG <sub>2000</sub>
No. 4	Modified with 1% chitosan

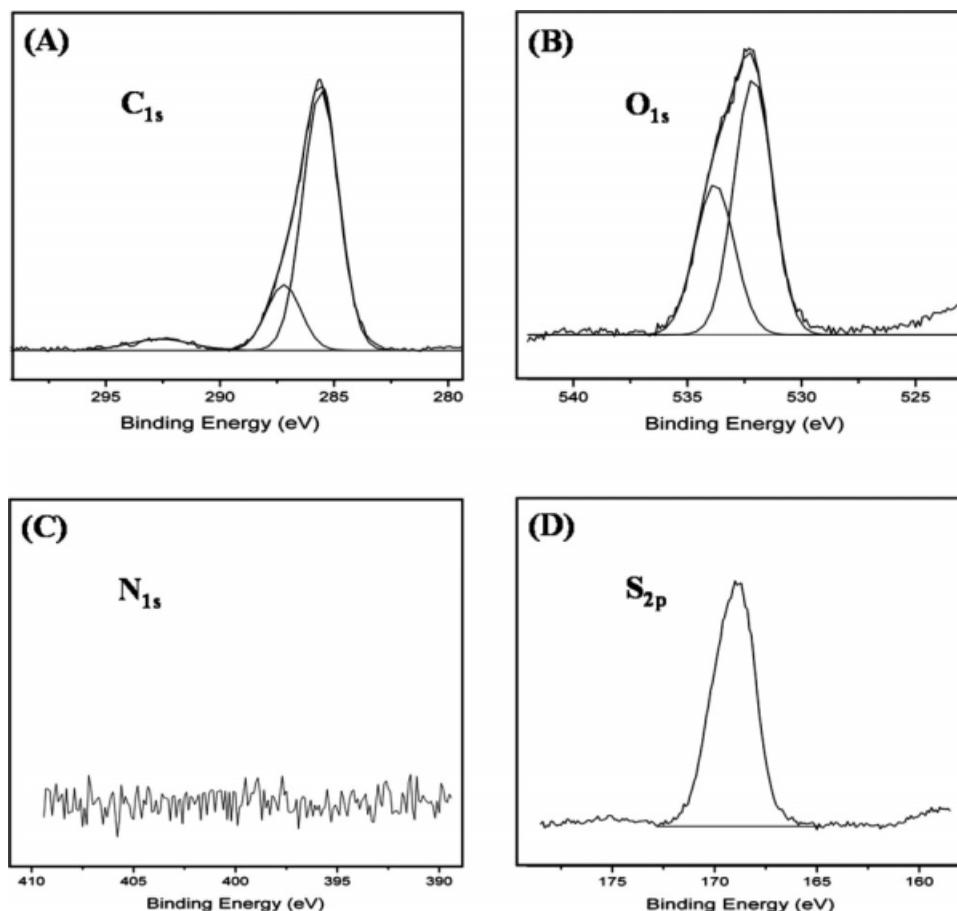
exhibit core-level binding energies of 285.16 eV for the C—H and C—C species, 286.57 eV for the C—O species, and 292.00 eV for the C—C species on the aromatic benzene rings, respectively [Fig. 6(A)]. The atom percentages are 50.01% for the C—C species, 17.47% for the C—S species, and 4.27% for the C—C species in aromatic benzene rings, respectively. The O<sub>1s</sub> core-level spectrum can be deconvoluted into two peaks components at 531.79 eV for the O=S species and 533.50 eV for the O—C species. The atom percentages are 14.66% for the O=S=O species and 7.33% for the O—C species. The S<sub>2p</sub> core-level spectrum of virgin PES membrane can be deconvoluted into one peak component with binding

**TABLE II**  
Relative Surface Atomic Concentration of the Virgin PES Membrane Calculated from XPS Spectra

Peak	Position	Assignment	Atoms percent (%)
C <sub>1s</sub>	285.16	—C—C—	50.01
	286.57	—C—S—	17.47
	292.00	Aromatic ring	4.27
O <sub>1s</sub>	531.79	O=S=O	14.66
	533.50	—O—C—	7.33
S <sub>2p</sub>	168.60		5.18

energy at 168.60 eV, this can be associated with the sulfone group of PES membrane. The atom percentage of sulfone is 5.18%.

Figure 7 shows the high-resolution C<sub>1s</sub>, O<sub>1s</sub>, N<sub>1s</sub>, and S<sub>2p</sub> XPS spectra of polyamide-/PVA-modified PES membrane surface by interfacial polymerization. The C<sub>1s</sub> core-level spectrum of polyamide-/PVA-modified PES membrane can be deconvoluted into three peak components with binding energies at 284.40 eV for the C—H and C—C species, at 285.89 eV for the C—O species and at 288.69 eV for the



**Figure 6** High-resolution (A) C<sub>1s</sub>, (B) O<sub>1s</sub>, (C) N<sub>1s</sub>, and (D) S<sub>2p</sub> XPS spectra of virgin PES membrane (No. 1).

TABLE III  
XPS Atomic Percent for Modified PES Membranes

Sample no.	XPS atoms percent				O/C	N/C	S/C
	C	O	N	S			
No. 1	71.75	21.99	–	5.32	0.306	–	0.074
No. 2	62.57	34.80	2.11	0.52	0.556	0.034	0.008
No. 3	68.15	24.17	6.92	0.76	0.355	0.102	0.011
No. 4	57.88	34.69	5.92	1.34	0.599	0.102	0.023

C=O species. The new peak component at the binding energy of 288.69 eV is assigned to the C=O species of the synthesized polyamide in polyamide-/PVA-modified PES membrane. The O<sub>1s</sub> core-level spectrum of polyamide-/PVA-modified PES membrane surface by interfacial polymerization can be deconvoluted into three peak components with binding energies at 531.05 eV for the O–S and O–H species, at 532.02 eV for the O=C species, and at 533.40 eV for the O–C species. The new peak component at the binding energy of 532.02 eV is assigned to the O=C species of the synthesized polyamide in polyamide-/PVA-modified PES membrane. The new

peak in the N<sub>1s</sub> core-level spectrum of polyamide-/PVA-modified PES membrane can be deconvoluted into two peak components with binding energy at 399.36 and at 400.83 eV, which are associated with amide groups. The new N<sub>1s</sub> core-level spectrum verifies that polyamide layers have been fabricated successfully on the PES membrane surface by interfacial polymerization. Sulfur was still observed in the spectrum of polyamide-/PVA-modified PES membrane surface. The S<sub>2p</sub> core-level spectrum of polyamide-/PVA-modified PES membrane can be deconvoluted into one peak components with binding energy at 168.60 eV, and this can be taken as the

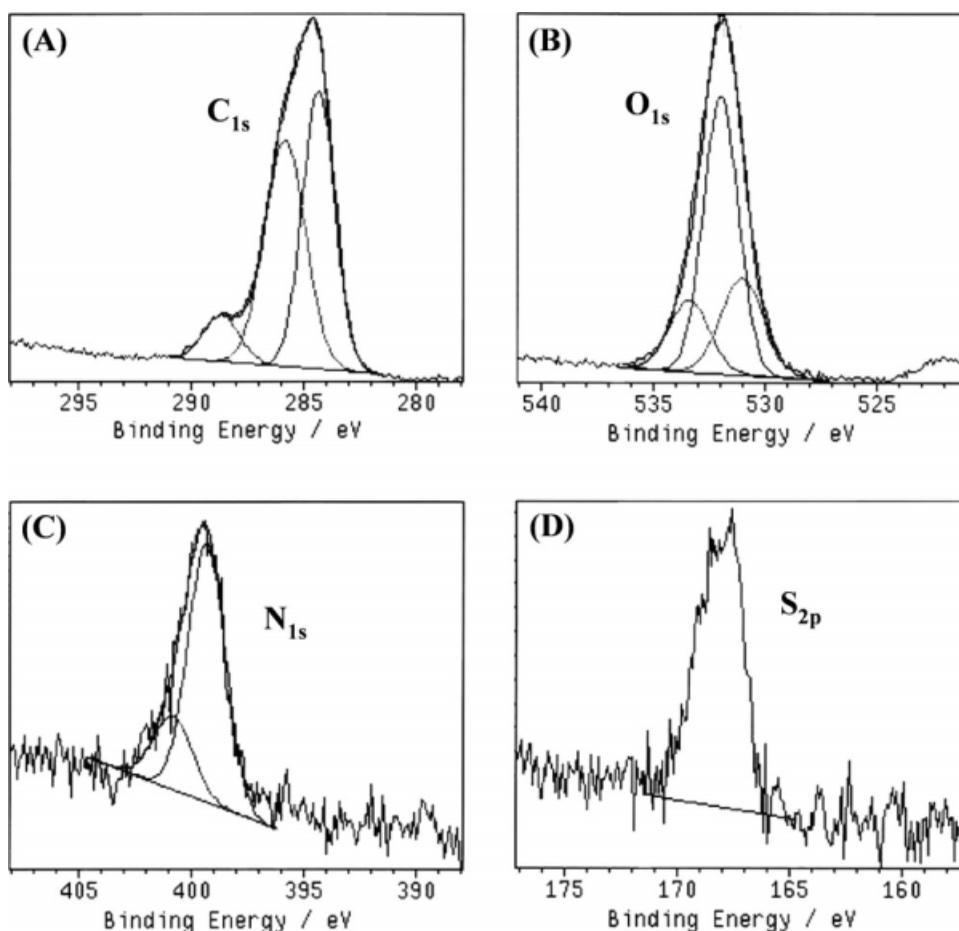
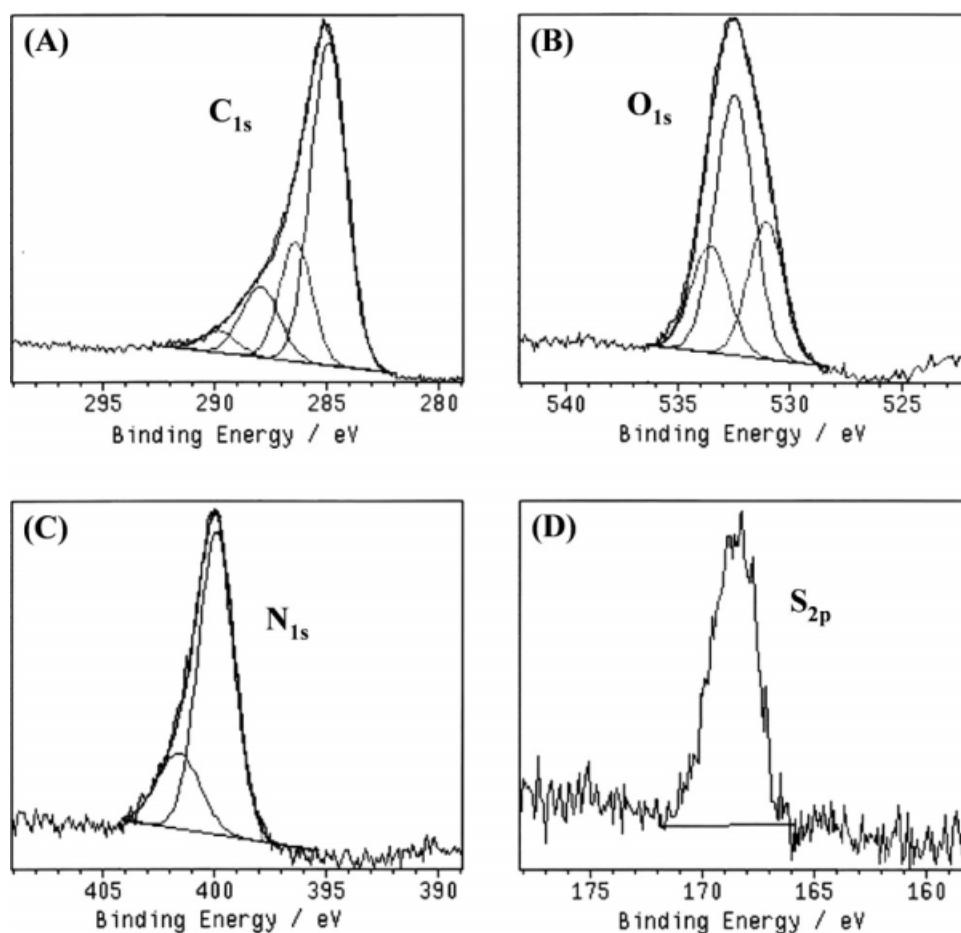


Figure 7 High-resolution (A) C<sub>1s</sub>, (B) O<sub>1s</sub>, (C) N<sub>1s</sub>, and (D) S<sub>2p</sub> XPS spectra of PVA/polyamide formed PES membrane by interfacial polymerization (No. 2).



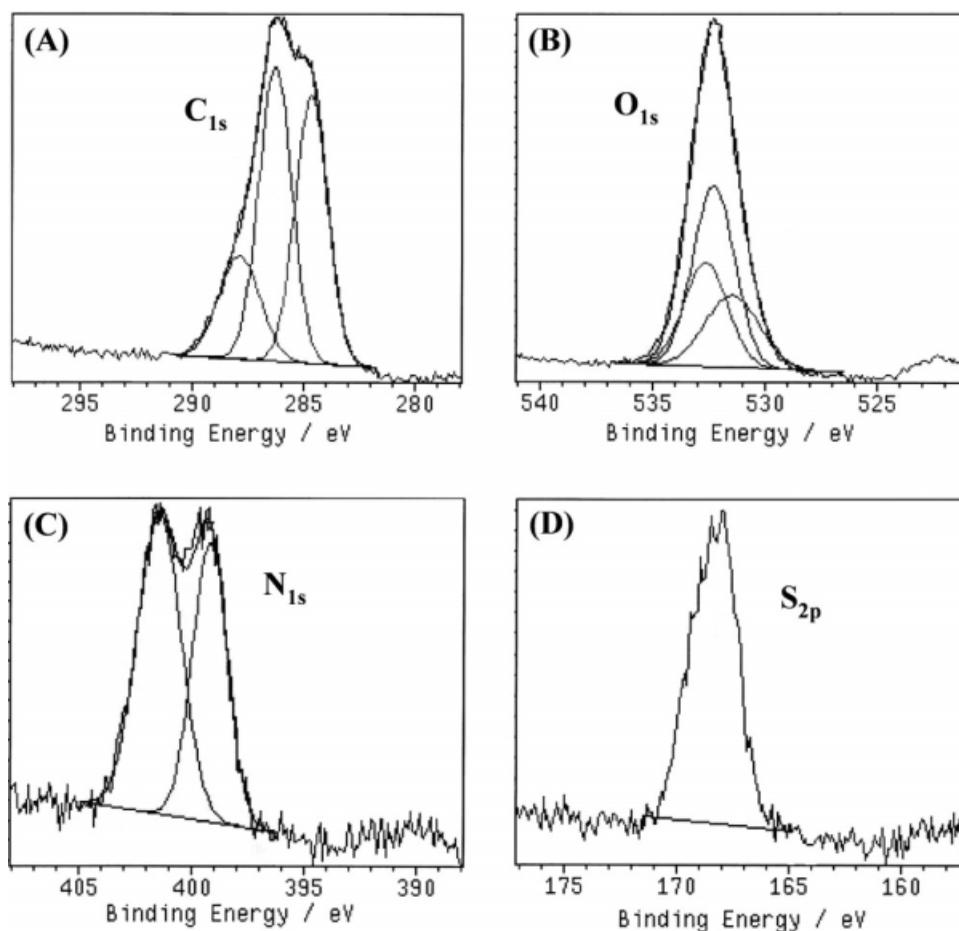
**Figure 8** High-resolution (A)  $C_{1s}$ , (B)  $O_{1s}$ , (C)  $N_{1s}$ , and (D)  $S_{2p}$  XPS spectra of PEG/polyamide formed PES membrane by interfacial polymerization (No. 3).

characteristic of the sulfone group of PES membrane. This result indicates that the membrane surface was not thoroughly covered by the thick polyamide layer with PVA, but polyamide/PVA layers clearly occurred on the PES membrane.

Figure 8 shows the high-resolution  $C_{1s}$ ,  $O_{1s}$ ,  $N_{1s}$ , and  $S_{2p}$  XPS spectra of polyamide-/PEG<sub>2000</sub>-modified PES membrane surface by interfacial polymerization. The  $C_{1s}$  core-level spectrum of polyamide-/PEG<sub>2000</sub>-modified PES membrane can be deconvoluted into four peak components with binding energies at 284.95 eV for the C–H and C–C species, at 286.41 eV for the C–O species, and at 287.99 and at 289.93 eV for the C=O species. The new peak components at the binding energy of 287.92 and 289.93 eV are assigned to the C=O species of the synthesized polyamide in polyamide-/PEG<sub>2000</sub>-modified PES membrane. The  $O_{1s}$  core-level spectrum of polyamide-/PEG<sub>2000</sub>-modified PES membrane surface by interfacial polymerization can be deconvoluted into three peak components with binding energies at 531.10 eV for the O–S and O–H species, at 532.52 eV for the O=C species, and at 533.60 eV for the O–C species. The new peak component at the bind-

ing energy of 532.52 eV is assigned to the O=C species of the synthesized polyamide in polyamide-/PEG<sub>2000</sub>-modified PES membrane. The new peak in the  $N_{1s}$  core-level spectrum of polyamide-/PEG-modified PES membrane can be deconvoluted into two peak components with binding energy at 399.94 and at 401.60 eV, which are associated with amide groups. The new  $N_{1s}$  core-level spectrum verifies that polyamide layers have been fabricated on the PES membrane surface by interfacial polymerization. Sulfur was still observed in the spectrum of polyamide-/PEG-modified PES membrane surface. The  $S_{2p}$  core-level spectrum of polyamide-/PEG-modified PES membrane can be deconvoluted into one peak components with binding energy at 168.30 eV, and this can be taken as the characteristic of the sulfone group of PES membrane. This result indicates that the membrane surface was not thoroughly covered by the thick polyamide layer with PEG, but polyamide/PEG layers clearly occurred on the PES membrane.

Figure 9 shows the high-resolution  $C_{1s}$ ,  $O_{1s}$ ,  $N_{1s}$ , and  $S_{2p}$  XPS spectra of polyamide-/chitosan-modified PES membrane surface by interfacial



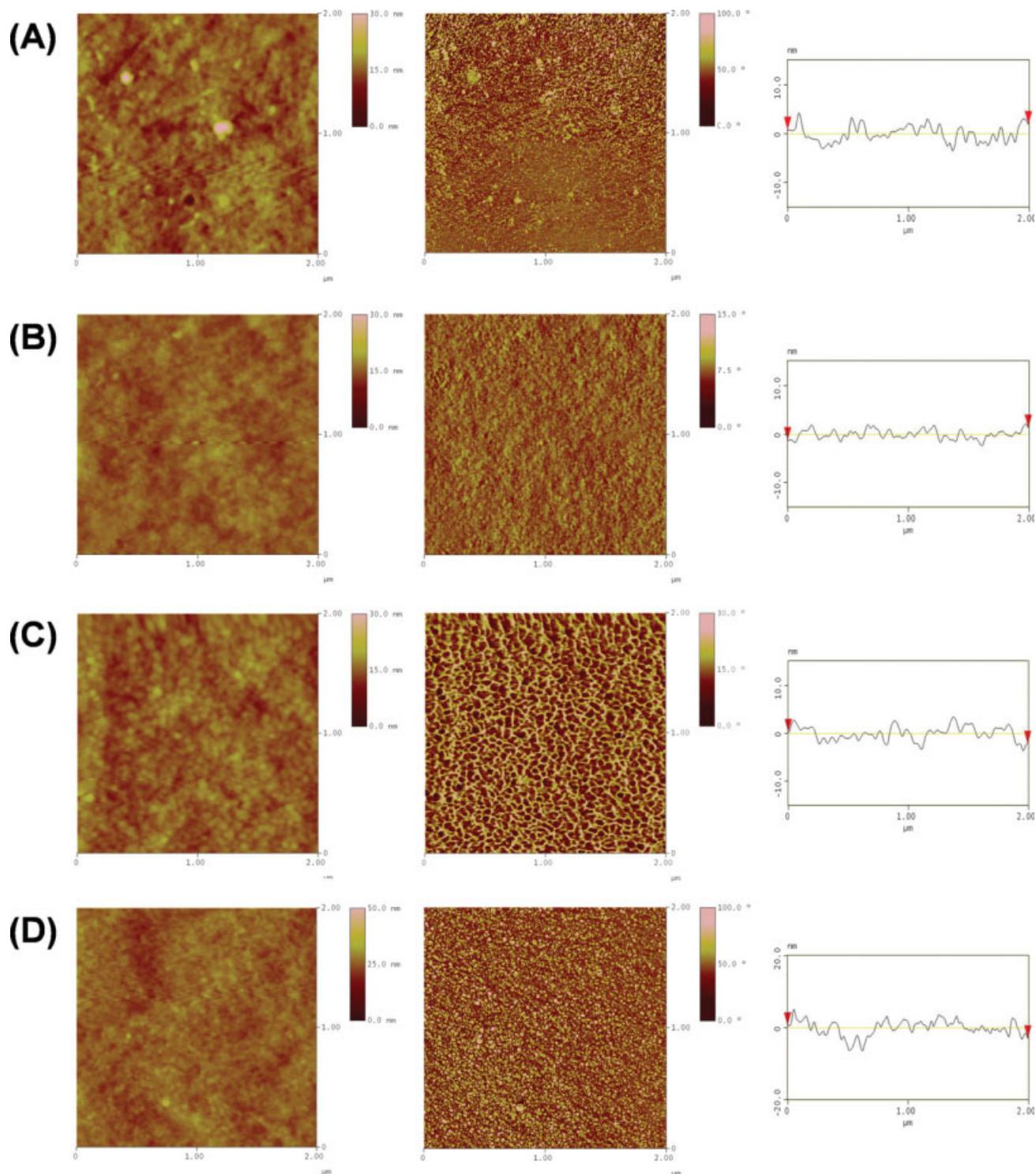
**Figure 9** High-resolution (A)  $C_{1s}$ , (B)  $O_{1s}$ , (C)  $N_{1s}$ , and (D)  $S_{2p}$  XPS spectra of chitosan/polyamide formed PES membrane by interfacial polymerization (No. 4).

polymerization. The  $C_{1s}$  core-level spectrum of polyamide-/chitosan-modified PES membrane can be deconvoluted into three peak components with binding energies at 284.71 eV for the C–H and C–C species, at 286.34 eV for the C–O species, and at 287.92 eV for the C=O species. The new peak component at the binding energy of 287.92 eV is assigned to the C=O species of the synthesized polyamide in polyamide-/chitosan-modified PES membrane. The  $O_{1s}$  core-level spectrum of polyamide-/chitosan-modified PES membrane surface by interfacial polymerization can be deconvoluted into three peak components with binding energies at 531.50 eV for the O–S and O–H species, at 532.67 eV for the O=C species, and at 533.34 eV for the O–C species. The new peak component at the binding energy of 532.67 eV is assigned to the O=C species of the synthesized polyamide in polyamide-/chitosan-modified PES membrane. The new peak in the  $N_{1s}$  core-level spectrum of polyamide-/chitosan-modified PES membrane can be deconvoluted into two peak components with binding energy at 399.23 and at 401.47 eV, which are associated with amide groups of polyamide layer and amine groups of chitosan. The new

$N_{1s}$  core-level spectrum verifies that polyamide layers have been fabricated successfully on the PES membrane surface by interfacial polymerization. Sulfur was still observed in the spectrum of polyamide-/chitosan-modified PES membrane surface. The  $S_{2p}$  core-level spectrum of polyamide-/chitosan-modified PES membrane can be deconvoluted into one peak components with binding energy at 168.00 eV, and this can be taken as the characteristic of the sulfone group of PES membrane. This result indicates that the membrane surface was not thoroughly covered by the thick polyamide layer with chitosan, but polyamide/chitosan layers clearly occurred on PES membrane.

Table III shows the XPS atomic percent and the ratio of O/C, N/C, and S/C for modified PES membranes. Generally, the carbon composition was decreased, and the oxygen composition was increased by surface modification. Polymeric membrane surface might have become more hydrophilic with more oxygen components, which could interact with water molecules.

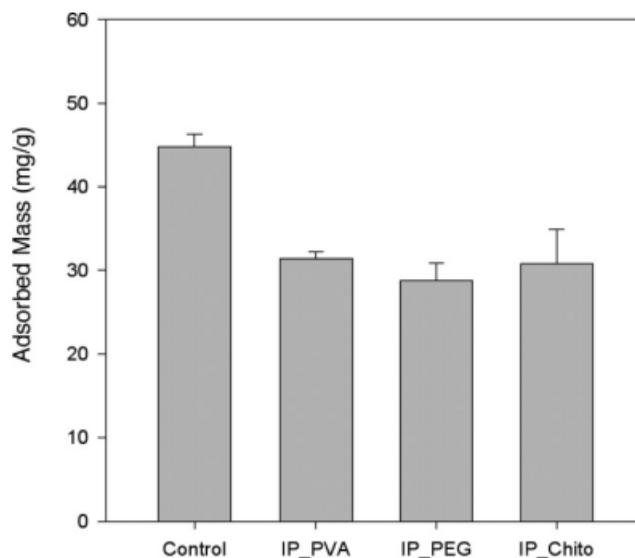
Figure 10 represents AFM surface images of virgin PES and all modified PES membranes with a



**Figure 10** AFM topography, phase image, and cross-sectional roughness of thin-film composites by interfacial polymerization: (A) virgin PES membrane (No. 1), (B) film composite with PVA (No. 2), (C) film composite with PEG (No. 3), and (D) film composite with chitosan (No. 4). The root mean square roughness is (A) 2.1 nm, (B) 1.2 nm, (C) 1.5 nm, and (D) 2.0 nm. Image size is  $2 \mu\text{m} \times 2 \mu\text{m}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).

projection area of  $2 \mu\text{m} \times 2 \mu\text{m}$ , in which the unique and characteristic ridge-and-valley structure of the PES membranes is clearly shown. The bar indicates the vertical deviations in the membrane surface; the

white region indicates the highest level, and the dark region indicates the lowest level. The surface of the virgin PES membrane is not homogeneous but heterogeneous, whereas modified PES membranes



**Figure 11** Mass of the  $\beta$ -lactoglobulin adsorbed on the unmodified and modified PES membranes by static adsorption experiment. The concentration of  $\beta$ -lactoglobulin was 2.5 mg/mL and the solution pH was 3.0.

have more or less lower roughness than the virgin PES membrane.

#### Protein adsorption on modified membranes

Static adsorption of  $\beta$ -lactoglobulin on the modified PES membrane surface was studied to compare the decrease in the amount of adsorption on the modified PES membranes. As shown in Figure 11, the amount of  $\beta$ -lactoglobulin adsorbed on the PES membrane was reduced from 30 to 35% by surface modification. Among the modified PES membranes, PEG-modified membrane showed lowest protein adsorption. Although this membrane showed highest contact angle among modified membranes, the hydrophobic interaction between protein and modified PES membrane should be the lowest. However, membranes modified with chitosan did not show lowest protein adsorption among the modified PES membranes even though the contact angle of this membrane showed the lowest value. The correlation between contact angle and the amount of adsorbed protein was not well established, but all three modified membranes showed lower protein adsorption than the virgin PES membrane. The differences of protein adsorption among all modified PES membrane surfaces are statistically insignificant; it is difficult to assign levels of vulnerability of protein adsorption onto modified PES membrane surfaces based solely on values of the contact angles, particularly the differences of contact angles are not significant (see Fig. 4). It is widely known that the tendency of protein adsorption onto polymeric mem-

branes is determined not only by hydrophilicities but also by other factors.<sup>23,25</sup>

#### CONCLUSIONS

To reduce the protein adsorption on polymeric membrane, PES membrane was modified by a surface modification technique: TFC by interfacial polymerization. This modification method is an effective technique to improve the hydrophilicity of polymeric membranes. PVA, PEG, and chitosan were used to modify the surface of PES membranes because of their excellent hydrophilic property. Surface properties of modified PES membranes were characterized by contact angle, FTIR, XPS, and AFM. The instrument measurements indicated that the hydrophilic modification of the PES membrane was successfully achieved by interfacial polymerization. Static adsorption experiment showed that modified membranes have more hydrophilic surface and reduce the amount of protein adsorption by 30–35%. This outcome shows that modification of PES membranes by interfacial polymerization is an effective technique to improve the hydrophilicity of PES membranes. This study has demonstrated that PVA, PEG, and chitosan all showed favorable result in modifying PES membrane for fouling reduction. This method would improve the current technology for separating food ingredients and fractionating high-value substances from food processing byproducts.

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